SCIENCE FOR GLASS PRODUCTION

CHARACTERISTICS OF THE CHANGES IN THE DEFORMATION PROPERTIES OF GLASS-FORMING MELTS

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The basic principles of rheology are stated. The basic rheological properties during flow and some structural characteristics of silicate glass-forming melts are presented. The characteristics of the changes occurring in the deformation properties of molten glass during the manufacture of glass articles, specifically, glass containers, are indicated.

Key words: rheology, viscosity, shear stress, deformation, formation of glass articles, defects in glass articles.

The determining factor in the formation of articles from glass-forming melts is rate at which glass solidifies. The solidification rate is determined by the aggregate of all changes occurring in the viscosity over time. In the process changes occur in the structure, properties, and characteristics of melts.

The changes occurring in the structural – mechanical properties and the properties of materials systems are due to the interactions between the structural elements and the medium as well as with each other. The methods of rheology — the science of stresses, deformations, and flows of material systems — make it possible to investigate these properties. Rheology studies the properties of systems in terms of deformations under external loads [1 – 3].

One can also study the conditions under which the appearance and relaxation of stresses occur in the corresponding systems. This is very important for glass technology. During the formation of glass articles nonuniform cooling results in the appearance of stresses which must be decreased to a safe level by annealing.

We shall examine the character and interrelation of rheological factors in application to glass melts and the formation of glass articles.

Viscosity is one of the most important structural and technological characteristics of glass-forming melts [3, 4].

It has been established that to each temperature there correspond completely definite values of the viscosity and an equilibrium structure of the melt, which, however, is not established immediately but rather over the relaxation time. Relaxation phenomena are clearly manifested for glass-forming melts and, especially, at a transition to a solid, glassy state; this is due to the considerable viscosity.

The viscosity of glass-forming melts and glasses varies over a wide range. The equilibrium values of the viscosity at low temperatures are established over a long time. In this connection the particulars of the changes occurring in the thermal and deformation properties of glass-forming melts are manifested quite clearly in the technological processes involved in glass production, specifically, in the non-isothermal formation of articles, for example, glass containers. In a number of cases this results in articles being scrapped.

Principles of Rheology. In rheology, deformations (elastic and residual) are basic characteristics of a system. Two forms of deformations are distinguished: tension (compression) and shear. All other forms of deformation can be represented by combinations of these basic forms. As a rule, the indicated deformations occur under normal and tangential stresses.

Rheological models are used to study the behavior of materials systems under forces and engendered stresses all acting in definite directions [1 – 3]. Basically, the rheological characteristics of systems, including glassy systems, can be represented by four types of models: an ideally elastic Hooke body (spiral spring); an ideally viscous Newtonian liquid (piston with openings, which is placed in a cylinder containing a liquid); a viscoelastic Maxwellian liquid (Hooke and Newtonian elements connected in series); and, a viscoelastic

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Kelvin – Voigt body (Hooke and Newtonian elements connected in parallel).

The rheological properties and characteristics of real bodies, including glass bodies, can be modeled by various combinations of the ideal models listed above.

For an ideally elastic Hooke body the deformation γ is proportional to the shear stress δ:

$$\gamma = \delta/E,$$

where E is Young's modulus.

An ideally viscous Newtonian liquid flows in accordance with Newton's law: the shear stress δ in a laminar flow of a liquid with viscosity η is proportional to the gradient of the flow velocity υ or the deformation rate γ^*:

$$\delta = \eta d\upsilon/dy = \eta d\gamma/d\tau = \eta\gamma^*,$$

where $\gamma^* = d\gamma/d\tau$ is the rate of shear deformation.

A viscoelastic Maxwellian liquid is of greatest interest for instantaneous and fixed deformation ($\gamma = \text{const}$ and $\gamma^* = 0$). The internal stress that arises here gradually decreases with time (relaxes) as a result of the deformation of the viscous element. Under such conditions, after suitable transformations,

$$\ln \delta/d_0 = - E\tau/\eta$$

or

$$\delta = \delta_0 \exp (- \tau/\tau^*),$$

where $\tau^* = \eta/E$ is the stress relaxation time.

This equation shows that the difference between liquids and solids is not sharp and is of a kinetic, relaxation character. For example, if the relaxation time is much longer than the time over which stress acts, then this is characteristic for solids. If the relaxation time is shorter than the time over which stress acts, then the body behaves like a liquid — the stresses decrease as a result of the flow of the liquid.

Thus, the behavior of a body is determined by the time over which stresses act relative to the relaxation time. This can be illustrated with the following examples. If the time of action on a typical liquid — water — is less than the relaxation time, then there is no enough time for flow to occur and the liquid behaves as an elastic solid. A bullet splits a stream of water ($\eta = 10^{-3}$ Pa · sec, $E = 10^{10}$ Pa, $\tau^* = 10^{-13}$ sec) as it would a brittle solid. When molten glass, which is an example of a liquid with a higher viscosity, is fed into a molding machine to be formed into an article and is sheared in the feeder, before the glass drop finally separates from the main mass a thin layer fractures like a brittle solid body.

A Kelvin – Voigt viscoelastic solid characterizes the capability of a body to regain its properties after a load is removed. In such a body the deformation γ under a constant load (stress) δ_0 develops in time. The deformation reaches its maximum value when the deformation rate decreases to zero. If the stress is removed after a definite maximum deformation is reached, then the system likewise returns to its initial state within a definite time. Here

$$\gamma = \gamma_0 \exp (- E\tau/\eta) = \gamma_0 \exp (- \tau/\tau^{**}),$$

where $\tau^{**} = \eta/E$ is the relaxation time of the deformation, characterizing the elasticity of the body.

All forms of rheological properties examined above appear for glass melts at different temperatures, right up to the transition into a glassy state [2]. Relaxation can occur over a time ranging from several seconds to several hours or more, since viscosity increases significantly with decreasing temperature. Maxwell's simple model is applicable only for estimating the order of magnitude of the relaxation time, but even it does not describe adequately the behavior of real glass-forming melts. A more suitable model can be obtained by using different combinations of the Maxwell and Kelvin – Voigt elements. However, the more complicated models have not one but several relaxation times (a spectrum of relaxation times), which, of course, complicates the description of the process.

Some Structural Features of Glass-Forming Melts. Before examining the rheological characteristics of glass-forming melts, we must call attention to certain structure features which such melts manifest under deformation.

Commercial silicate glasses are characterized by the presence of a quite rigid silicon – aluminum – oxygen framework in which the alkali and alkaline-earth metal ions are randomly distributed. The structure of silicate glasses is also characterized by the presence of regions of micro-nonuniformities. Silicate-glass melts retain their spatial framework at high temperatures; but, the framework becomes more mobile, including because its connectedness decreases. A definite connectedness of the framework is due mainly to Si – O bonds.

Evidently, together with the spatial network of chemical bonds there exists a spatial network of physical bonds. It can be termed a fluctuation network by analogy to organic polymers. The nodes of a fluctuation network are regions of nonuniformity which are connected with one another by physical bonds. The thermal motion of the structural elements changes the fluctuation spatial network whose nodes are constantly breaking down and being restored, i.e., the network is in a state of dynamical equilibrium. The fluctuation network possesses a definite elasticity and resists deforming forces. The higher the deformation rate, the more the fluctuation network breaks down. After these forces stop acting a certain amount of time is always required for the destructive processes to reach a dynamical equilibrium and for the nodes of the fluctuation network to be restored.

A deformation of any magnitude changes the structure of the melt in a viscoelastic state, primarily as a result of the orientation of small structural elements and a definite level of destruction of the fluctuation spatial network. However, for

low deformation rates the equilibrium in the system shifts to such an extent in the direction of restoration of the destroyed structural formations that the structural changes still occurring do not appreciably affect the magnitude of the viscosity — the determining structural factor. Thus, the structure of a high-viscosity melt appears to remain constant; for this reason, the flow in this region of change of the shear stress and deformation rate conforms to Newton's law and the melt exhibits the properties of Newtonian liquids.

Rheological Properties and Flow of Glass-Forming Melts. The rheological flow curves for a high-viscosity glass-forming melt are shown in a general form in Fig. 1. For a large range of variation of the shear stress, deformation rate, and viscosity these curves are ordinarily plotted in logarithmic coordinates. For shear deformation

$$\delta = \eta \gamma^* \quad \text{or} \quad \log \delta = \log \eta + \log \gamma^*.$$

These equations express Newton's law or the flow law for ideal viscous liquids, whose rheological properties are uniquely determined by the viscosity. For small shear stresses (see Fig. 1a) a rectilinear section is observed on the flow curve. On the initial section (I) of the curve the flow is characterized by the highest value of the viscosity, denoted as η_0 and called the initial Newtonian viscosity. As the stress and correspondingly the shear rate increase, a transition occurs into a flow region where the shear rate increases to such an extent that there is enough time for only a part of the fluctuation spatial network that decomposed under shear to be restored. The larger the part of the fluctuation network that cannot be restored because there is not enough time, the smaller the viscous resistance to the flow, which is expressed by a decrease of the viscosity in the region II of the flow curve. This decrease is steeper on the plot of log η vs log δ than on the log η – log γ^* plot (see Fig. 1b and c).

As the shear rate increases, there comes a time when an increase of the shear rate no longer changes the viscosity; this corresponds to region III on the flow curve. The flow in this region is determined by the lowest value of the viscosity characteristic for the melt. This is the finite Newtonian viscosity η_f. Here the structure of the fluctuation network is largely destroyed. This means that there is insufficient time for the fluctuation network to be restored for such a shear rate. Thus the region III on the flow curve is a region of flow where the structure of the fluctuation network is largely destroyed.

The effect of the rheological properties on the flow can be studied in two basic regimes: $\delta =$ const, $\gamma^* \neq$ const or $\gamma^* =$ const, $\delta \neq$ const. In addition to using these two static-deformation methods, high-viscosity melts can also be studied in a dynamic regime of deformation, i.e. by applying a force that is a sinusoidal function of time (elastic oscillations). This method reveals the viscoelastic behavior of the high-viscosity melts quite clearly. In this case it is assumed that the frequency with which the force acts in the dynamical re-
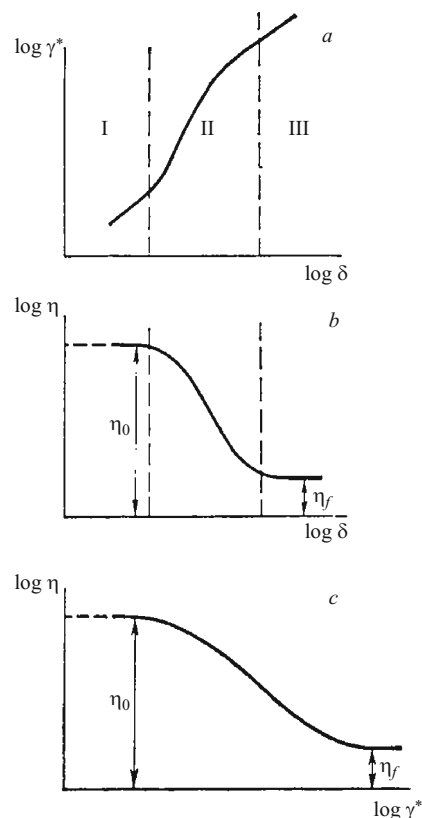
Fig. 1. Rheological flow curves for a high-viscosity glass-forming melt: a) shear rate versus shear stress; b, c) viscosity versus stress and shear rate.

gime is equivalent to the rate of shear in a regime with flow at constant velocity or under constant stress. The dependence of the viscosity η on the forcing frequency ω (elastic oscillations) is analogous to the dependence on the viscosity on the shear rate (see Fig. 1).

For low frequencies (just as for low shear rate) there is sufficient time for the fluctuation network to re-appear over one deformation cycle. In this region the viscosity assumes its highest value and is analogous to the highest Newtonian viscosity η_0. The ratio η_τ / η_0 of the running to the initial viscosity in this frequency range is equal or close to 1. As frequency increases, viscosity decreases as compared with the initial value and the viscosity ratio presented above decreases. At the same time as the viscosity decreases, the elastic modulus increases. The increase of the elastic modulus with increasing forcing frequency or with increasing deformation rate is characteristic for all physical states of glass. It is obvious that the elastic modulus and the viscosity decrease with increasing temperature.

Relaxation Phenomena in Glass-Forming Melts Subject to Elastic Oscillations. The internal parameters of a high-viscosity melt change when it is subject to elastic oscillations, specifically, the fluctuation spatial network breaks down and the melt transitions from a state with viscosity η_0 into a stable "perturbed" state with a lower viscosity (see
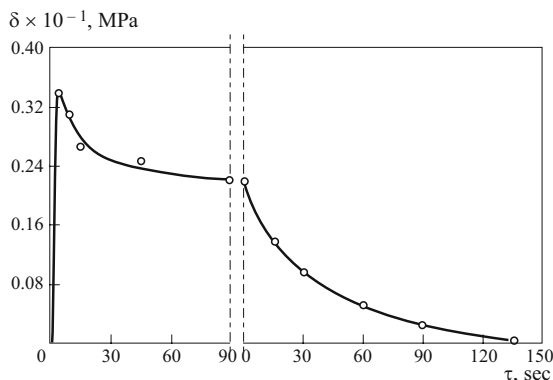
Fig. 2. Kinetics of the shear rate variation in glass-forming melt under elastic oscillations.

Fig. 3. Kinetic curve of the relaxation of the viscosity of a melt.

Fig. 1*b*). After the elastic oscillations stop, a relaxation transition of the melt back into the previous equilibrium state with viscosity η_0 is observed.

The action of elastic oscillations on glass melts and the rheological properties of melts have been investigated. The viscosity and relaxation properties of melts were evaluated using a rotation-type experimental apparatus with coaxial cylinders which was equipped with a vibrator that generated low-frequency vibrations [5].

It is characteristic for the shear stress to change when elastic oscillations with definite amplitude A stop and start. A complete curve of the change in the shear stresses in a lead-crystal (KhS-24) melt under the action of elastic oscillations is displayed in Fig. 2 (melt: $t = 1000°C$, $\eta = 1.38 \times 10^3$ Pa · sec; elastic oscillations: $\omega = 50$ sec^{-1}, $A = 3.5 \times 10^{-3}$ m). The molten glass was exposed to the action of elastic oscillations in a regime with a constant deformation rate ($\gamma^* = $ const).

A characteristic of this regime is that the deformation rate can be higher than the rate at which some nodes of extended framework formations in the melt break down. These nodes could be destroyed under the stresses developing in the molten glass during the initial period. But if the deformation rate is high, then there simply is not enough time for them to break down. As result, the stresses continue to increase, and only when they reach their maximum value does the relaxation time decrease under stresses to such an extent that there is enough time for the nodes of the framework formations in the melt to be destroyed at the given deformation rate. A definite destruction of the macrostructure of the melt in such an overstressed system results in a sharp drop of the stresses — from their maximum value to a constant value in the established regime. The left-hand side of Fig. 2 illustrates this clearly. The right-hand side of Fig. 2 characterizes the relaxation decrease of the stresses after the forcing oscillations stop.

The kinetic curve of the relaxation change of the viscosity of lead crystal (KhC-24) after elastic forcing oscillations
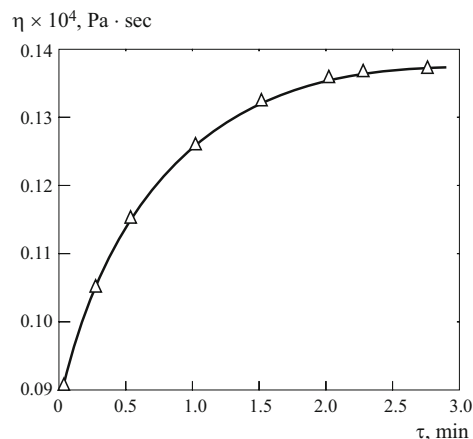
stop at 1000°C is presented in Fig. 3. The time variation of the viscosity in this case is characterized by the equation

$$d\eta/d\tau = (\eta_0 - \eta_\tau)/\tau^*, \qquad (1)$$

where η_0 is the initial value of the viscosity (before the elastic oscillations are introduced); η_τ is the value of the viscosity at a definite moment in time; τ is the time; and, τ^* is the relaxation time.

The solution of Eq. (1) for a definite moment in time has the form

$$\eta_\tau = (\eta_0 - \Delta\eta) \exp(-\tau/\tau^*),$$

where $\Delta\eta$ is the difference between the initial viscosity and the viscosity in the field of elastic oscillations.

The relaxation processes occurring in silicate glass-forming melts depend on the structure of the melts. For example, in the system $Na_2O - SiO_2$ the more complex the silicate formations in the melt, the longer the relaxation time of the structure returning to the equilibrium state is. The kinetic hysteresis of viscosity can serve as an indicator of relaxation phenomena in the melt.

The magnitude of the kinetic hysteresis of the viscosity η_1 and η_2 when the action of the elastic oscillations starts and stops, respectively, was evaluated when the character of the relaxation phenomena in $Na_2O - SiO_2$ melts was investigated. It was determined that elastic oscillations have virtually no effect in $2Na_2O \cdot SiO_2$ melt while their effect increases in the series $Na_2O \cdot SiO_2 - Na_2O \cdot SiO_2 - Na_2O \cdot 4SiO_2$. Discrete silicon – oxygen tetrahedra $[SiO_4]$ exist in $Na_2O \cdot SiO_2$ melt, while an increase of the SiO_2 content results in the appearance of complicated silicon – oxygen groups and framework formations. These formations impart to the melt elastic properties which are manifested in an oscillatory field. In addition, the change in the factor $\log(\eta_2/\eta_1)$ is proportional to the complexity of the main structural formations of the melt (Fig. 4).

The action of the elastic oscillations on glass melts can be used to increase the efficiency of the technological processes in the manufacture of glass articles [6]. For example, when articles are formed by pouring and pressing in molds elastic vibrations allow complex shapes to filled for efficiently and increase the quality of the articles.

Characteristics of the Changes in the Deformation Properties of Molten Glass During Formation. These characteristics play an important role in non-isothermal formation of glass articles, specifically, glass containers.

Stresses in glass melt vanish rapidly in the formation temperature range. However, under certain conditions the actions of a load, taking account of the continuous solidification of the molten glass, temporary stresses can increase to magnitudes causing the glass to fracture.

The automated formation of glass containers is a two step process and is implemented in preliminary and final forms. First the neck is pressed with the aid of a punch (jars, bottles — blowing-pressing method) or a punch and compressed air (bottles — double blowing method) and gob is formed. Then the finished article is blown from the gob.

The most dangerous operation from the standpoint of the appearance of stresses is pressing the neck of a glass container. In this case, according to the principles set forth in [1, 7], the deformation properties can be determined from the following relations:

relative deformation:

$$\gamma = L/(R_2 - R_1);$$

average shear rate:

$$\gamma^* = L/\tau \, (R_2 - R_1);$$

stress:

$$\delta = \eta\gamma^*; \tag{2}$$

$$\delta = G_\tau \gamma, \tag{3}$$

where L is the travel distance of the punch or the molten glass; $R_2 - R_1$ is the gap between the punch and the mold; τ is the time during which the load acts; η is the viscosity; and, G_τ is the shear modulus (depends on the time with a definite viscosity).

The relative deformation and average rate of shear during pressing of the neck were calculated for several types of glass containers (bottles and jars). The stresses as a function of time were calculated using data on the time variation of the shear modulus G_τ for different viscosity of the glass [7]. The relation (2) was used to evaluate the stresses for long times and low viscosity and the relation (3) was used as the time intervals became shorter and the viscosity increased.

The computational results for the stress as a function of time with different values of the viscosity in the process of pressing the neck of a glass container show that in the region $10^3 - 10^5$ Pa · sec, which is characteristic for the start of for-
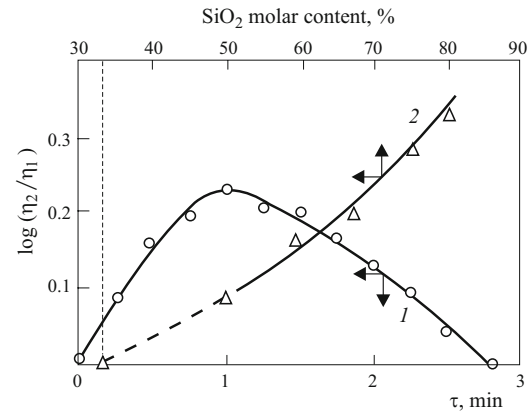
Fig. 4. Kinetic and concentration changes in the viscosity of glass-forming silicate melts in the field of elastic oscillations: *1*) kinetic hysteresis of the viscosity for $Na_2O \cdot SiO_2$ melt; *2*) hysteresis phenomena as function of the complexity of the main structural formations in the melt.

mation, no substantial stresses arise and the viscosity determines the magnitude of the stresses. The constancy of the stresses attests to this. But substantial stresses already arise in the region $10^6 - 10^7$ Pa · sec, and they grow with increasing viscosity and time of action and can cause the glass to fracture. During the formation of glass articles high-viscosity molten glass cools down and solidifies as a result of the complicated heat exchange with the surrounding medium with the participation of heat conduction and radiation. The following characteristics of the commercial formation process must be taken into account:

high-viscosity molten glass fed into the forming process is not completely chemically, thermally, and optically uniform;

cooling of molten glass during the formation process is nonuniform; this especially concerns the formation of articles in molds whose surface possesses a definite roughness; as a result of this, high-viscosity molten glass touches the heat-removing surface at a limited number of points;

cooling and solidification of molten glass starts from the surface and then propagates into the interior volume of the glass.

Taking account of these characteristics of molten glass and the conditions under which it cools down and solidifies it can be stated that viscosity changes will be fragmentary on the surface (fast process) as well as in the interior volume (slower process) [8]. Local nonuniformities of the viscosity of molten glass during fast and continuous solidification in combination with substantial local stresses and the character of their variation can give rise to foci of local fracture of the glass, first and foremost in the surface and adjoining layers ("splits"). Small "splits" can appear, for example, along the edge of pressed dishware and along the crown of the neck of bottles and jars. Cool down and solidification are most intense and substantial local stresses develop at these locations.

Ordinarily, "splits" appear because the temperature of the drop, neck rings, and punch are not high enough and the contact time between the punch and the glass is too long. A number of defects appearing in glass containers during formation are due to bugs in the operation of certain mechanisms of the glass-forming machines and molding sets (for example, "splits" under the crown of the neck). In this case the "splits" are due to an increase in the local mechanical loads on the surface of the glass.

On this basis it is necessary to ensure that sufficiently chemically uniform molten glass is obtained during the glassmaking process and that subsequently the molten glass is thermally uniform in the production line and feeder. At the same time it should be noted that for automated formation of hollow glass articles (glass containers, dishware, and others) the operating regimes of the feeder, the mechanisms of the glass-forming machine, and the molding sets can be regulated within definite limits so as to prevent the appearance or to eliminate diverse defects in the glass articles.

On the whole, the investigation of relaxation phenomena and the deformation properties of glass melts is one direction for studying their structure and for increasing the efficiency of various technological processes.

REFERENCES

1. V. E. Gul' and V. N. Kuleznev, *Structure and Mechanical Properties of Polymers* [in Russian], Vyssh. Shkola, Moscow (1972).
2. D. S. Sanditov and G. M. Bartenev, *The Physical Properties of Disordered Structures* [in Russian], Nauka, Novosibirsk (1982).
3. Yu. A. Guloyan, *Physical – Chemical Principles of Glass Technology* [in Russian], Tranzit-Iks, Vladimir (2008).
4. O. V. Mazurin and M. M. Shul'ts, *Modern Ideas Concerning the Structure and Properties of Glass* [in Russian], Nauka, Leningrad (1988).
5. V. V. Kupfer, Yu. A. Guloyan, and V. M. Zotov, "Investigation of the action of elastic oscillations on glass melt," in: *Production and Study of Glass and Silicate Materials* [in Russian], Verkhne-Volzhskoe Izd., Yaroslavl' (1974), Issue 4, pp. 68 – 75.
6. A. K. Mal'tseva, F. T. Gorobets, and S. M. Brekhovskikh, "Elastic oscillations as a technological factor acting on glass melt in the process of formation of glass articles," in: *Equipment and Technology for Obtaining Articles from Non-Metallic Materials* [in Russian], Moscow (1982), Pt. 2, pp. 60 – 67.
7. G. Mills, "The viscoelastic response of glass during forming," *Glass Technol.*, **14**(4), 101 – 105 (1973).
8. Yu. A. Guloyan, "On the theory of glass solidification," *Steklo Keram.*, No. 12, 3 – 6 (2004); Yu. A. Guloyan, "On the theory of glass solidification," *Glass Ceram.*, **61**(11 – 12), 395 – 398 (2004).